

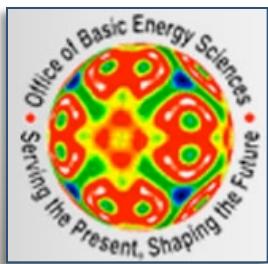


Predictive Unimolecular Kinetics for the Decomposition of Small Hydrocarbons and Hydrocarbon Radicals in Several Baths

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7th US National Technical Meeting
of the Combustion Institute

\$ DOE/OBES
Argonne-Sandia Consortium
on High Pressure
Combustion Chemistry
Combustion EFRC (J.A.M.)



Predictive unimolecular kinetics

From Troe

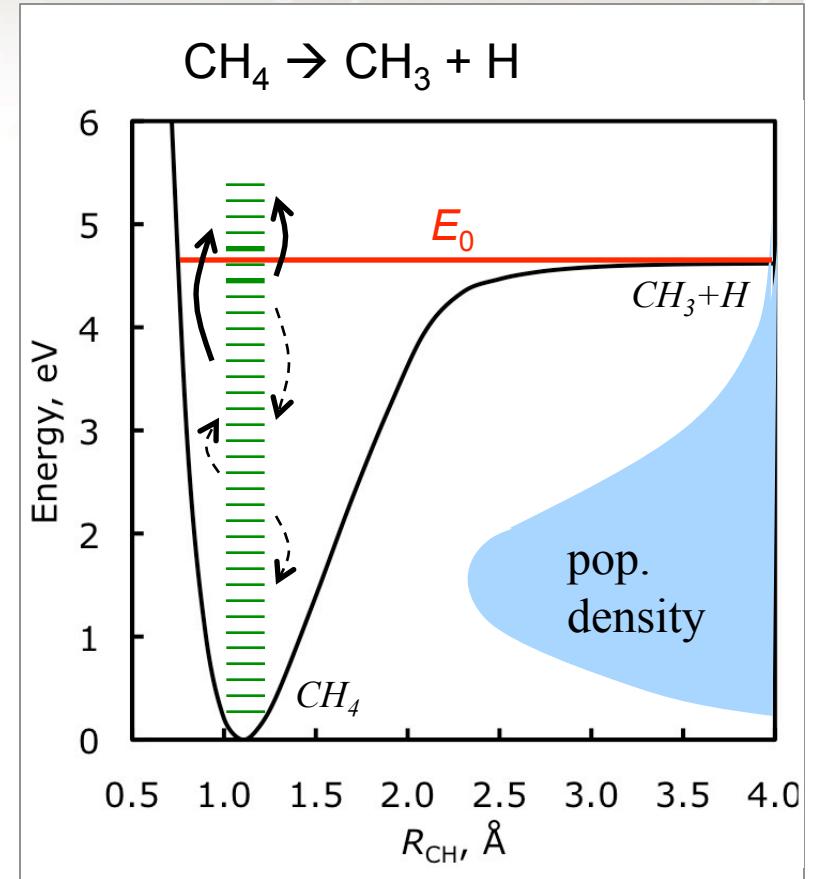
$$k_0 = \int_{E_0}^{\infty} dE' \int_0^{E_0} dE Z P(E' \leftarrow E) x(E)$$

collision rate steady state population
prob. of a collision knocking the system from internal energy E to E'
integrated over “reactive” collisions

$k_{ET} \approx \langle ZP \rangle = \langle R \rangle$

$$k_\infty = \int dE k_{TST}(E) f_{Boltz}(E)$$

$$k = \frac{k_\infty k_0 n_{bath}}{k_\infty + k_0 n_{bath}} F_b$$



Predictive calculations require
High level QC for E_0 , I_{rot} , ω_{vib} for ρ , f
VTST for k_{TST}
Some method for calculating k_{ET}



Predicting energy transfer

Master eq: Single exp down model

$$Z P(E' \leftarrow E) = Z N(E') e^{-(E'-E)/\alpha} \quad E < E'$$

with $E > E'$ from detailed balance.

$$\begin{aligned} \alpha &= \langle \Delta E_d \rangle \\ &= \alpha_{300} (T/300K)^n \end{aligned}$$

Typically empirically determined

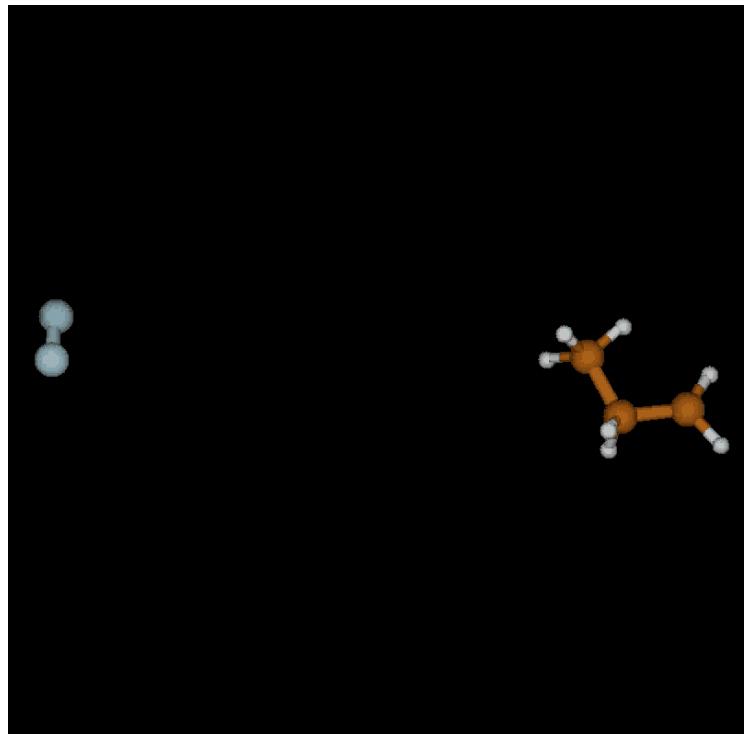
Classical trajectories

- Initial energy $\approx E_0$
- Thermal distributions for the bath
- Propagate ensembles of collisions
- Calculate $\alpha(T) = \langle \Delta E_d \rangle(T) \text{ cm}^{-1}$
 $\langle r_d \rangle = Z \langle \Delta E_d \rangle n_{1\text{Torr}} \text{ cm}^{-1}/\text{s}$
- Many similar studies in the literature

Potential energy surface

Major source of uncertainty

n-propyl + N₂





Potential energy surface

Direct dynamics

MP2/aug'-cc-pVDZ (+ accurate, – expensive)

Separable pairwise approximation

$V_{\text{full}} = V_{\text{target}}$ MP2/aug'-cc-pVDZ

+ V_{bath} Easy for atomic & diatomic baths

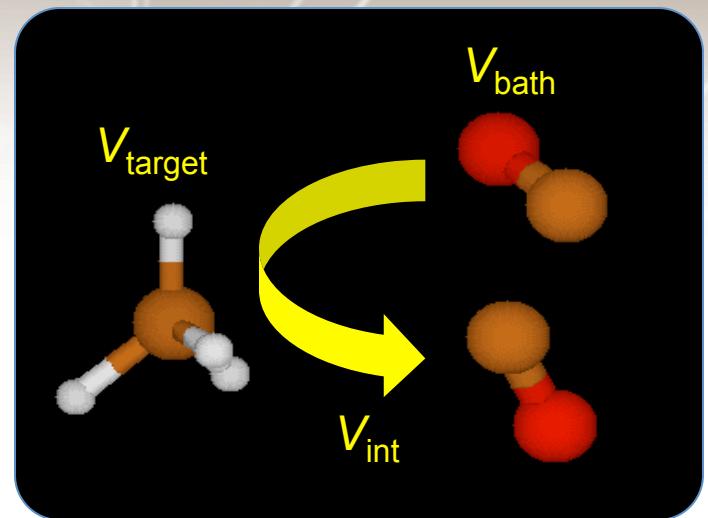
+ V_{int} $\approx \sum$ target atom-bath gas atom interactions

Parameterized against high level QC

Consider both Lennard-Jones (12/6)

and Buckingham (exp/6) interactions

(+ inexpensive & flexible, ? accurate)



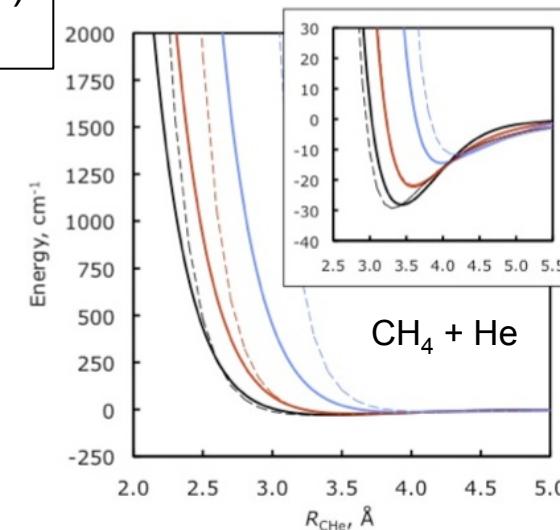
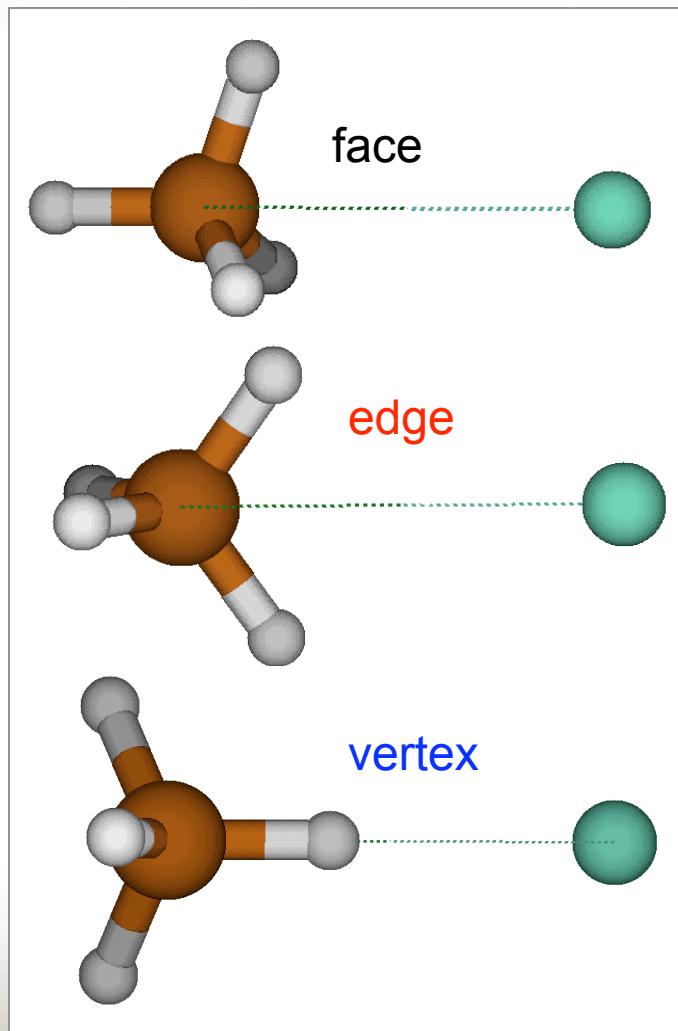
How accurate is the separable pairwise approximation?

Can we use cheaper methods for V_{target} ?

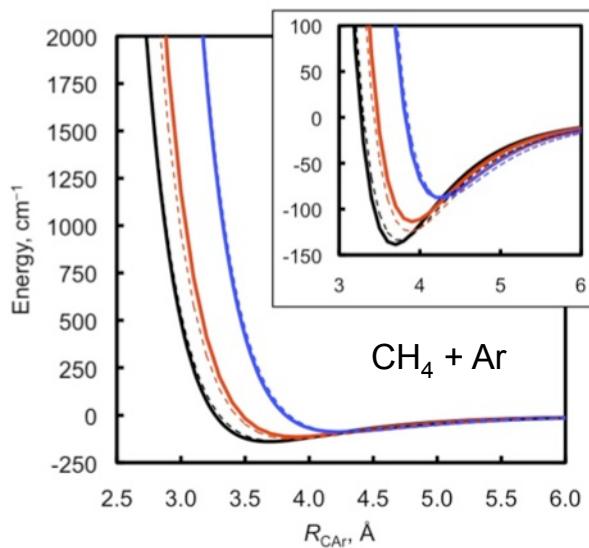
Can we obtain “universal” V_{int} parameterizations?



Fitting V_{int} for atomic baths



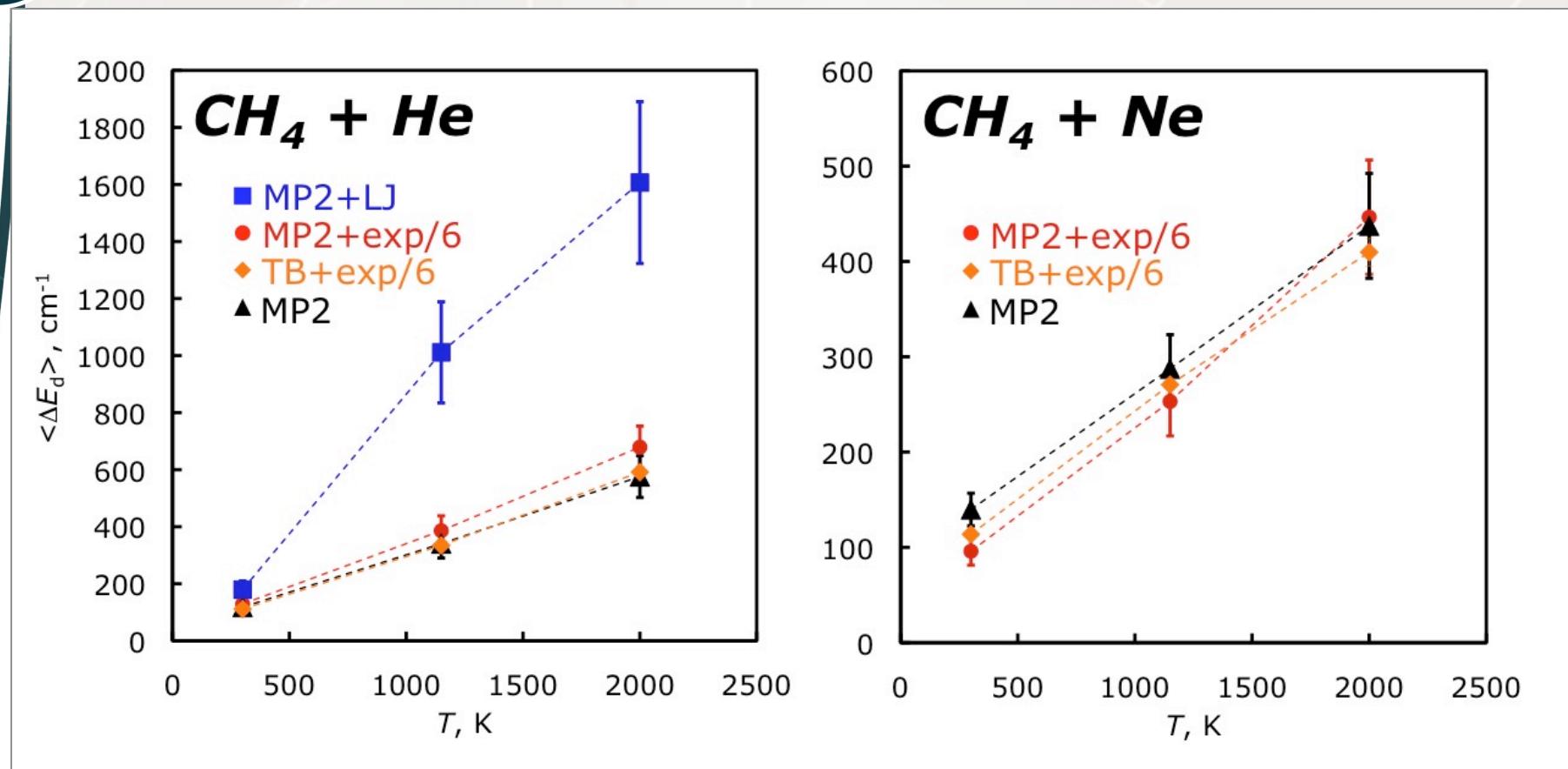
LJ (12/6)
Poor description of the repulsive wall



exp/6
Globally accurate for atomic baths



Tests of the separable pairwise method

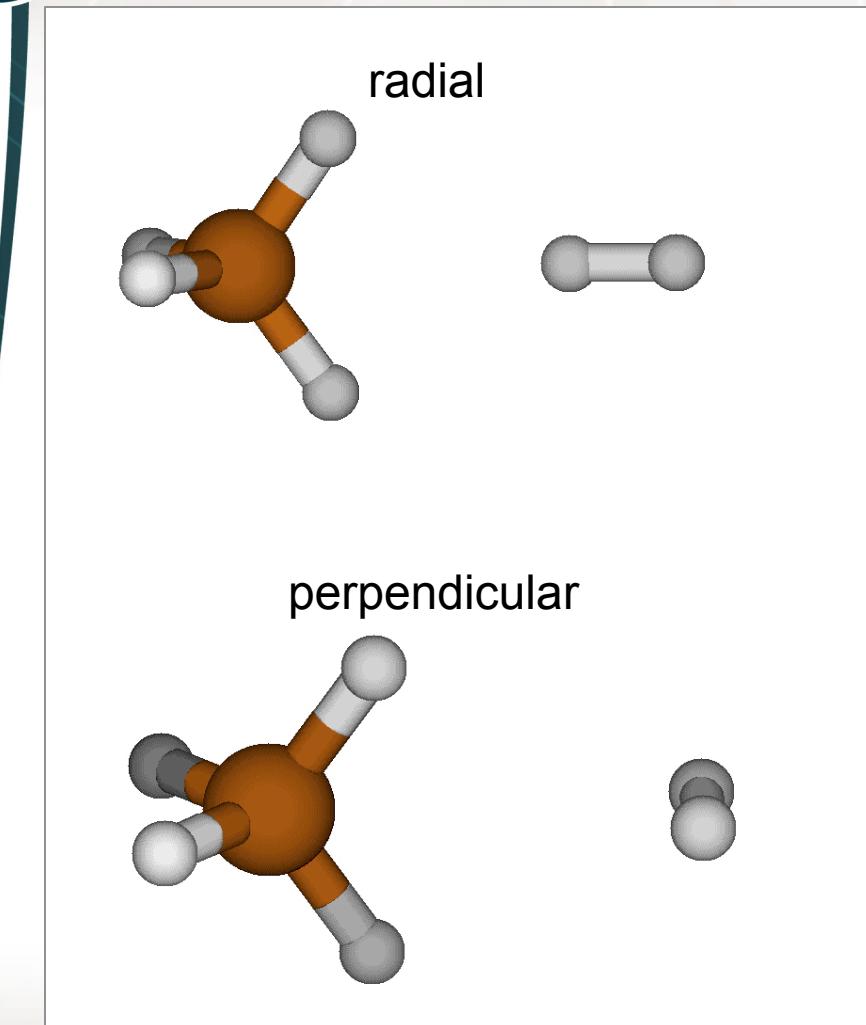


- ✓ LJ is confirmed to be inaccurate
- ✓ exp/6 is accurate for atomic baths
- ✓ TB: A cheap semiempirical description of the target works as well as MP2

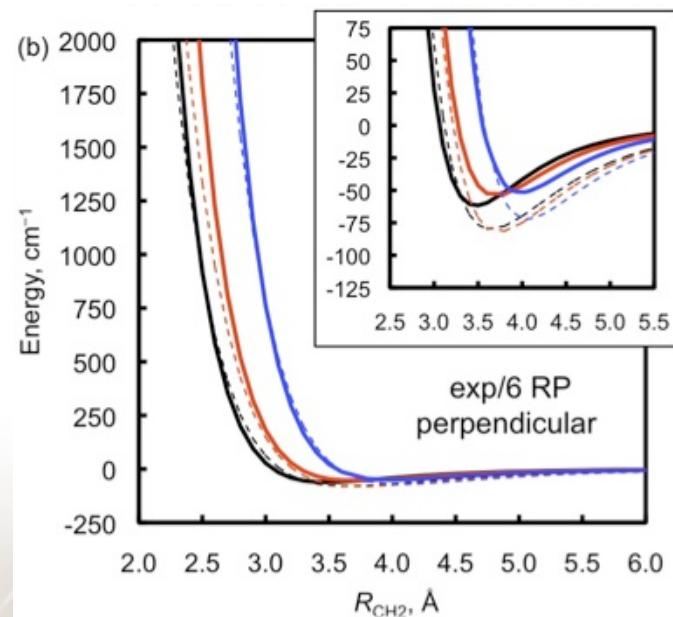
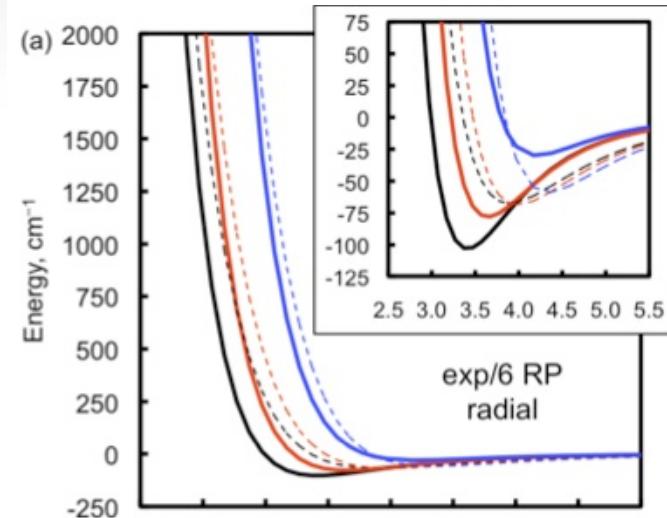
TB+exp/6 is >1000x faster than MP2!



Fitting V_{int} for diatomic baths

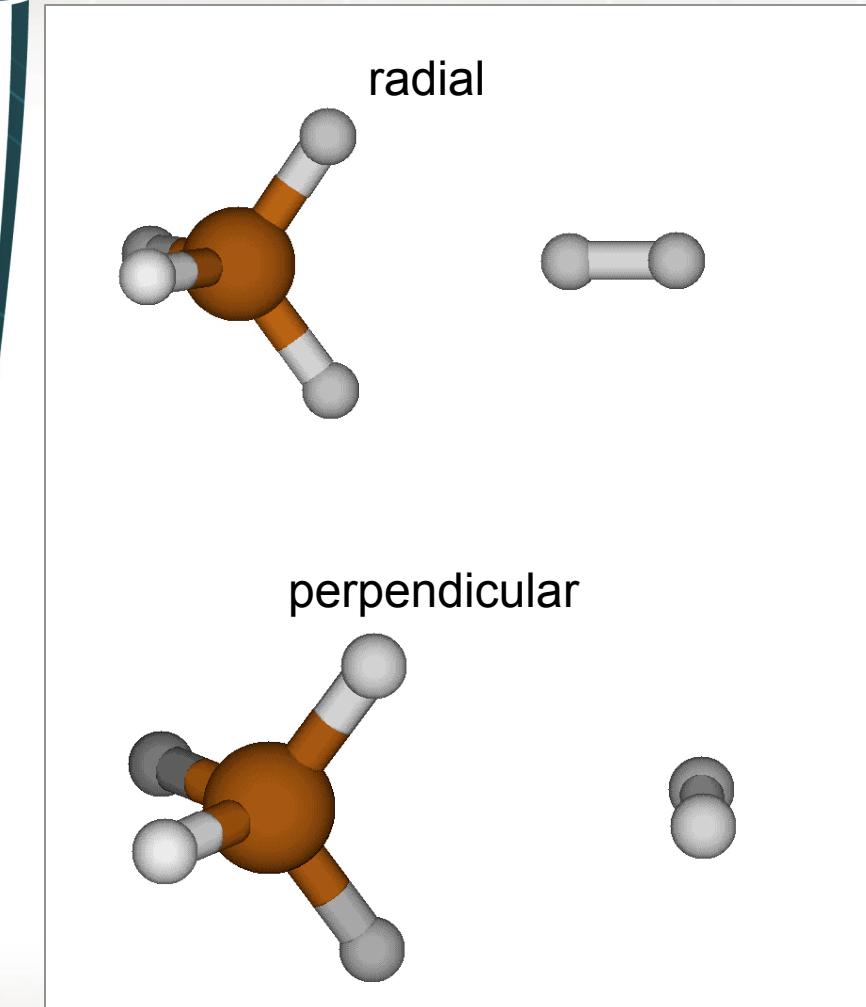


$\text{CH}_4 + \text{H}_2$: exp/6 fit to all data

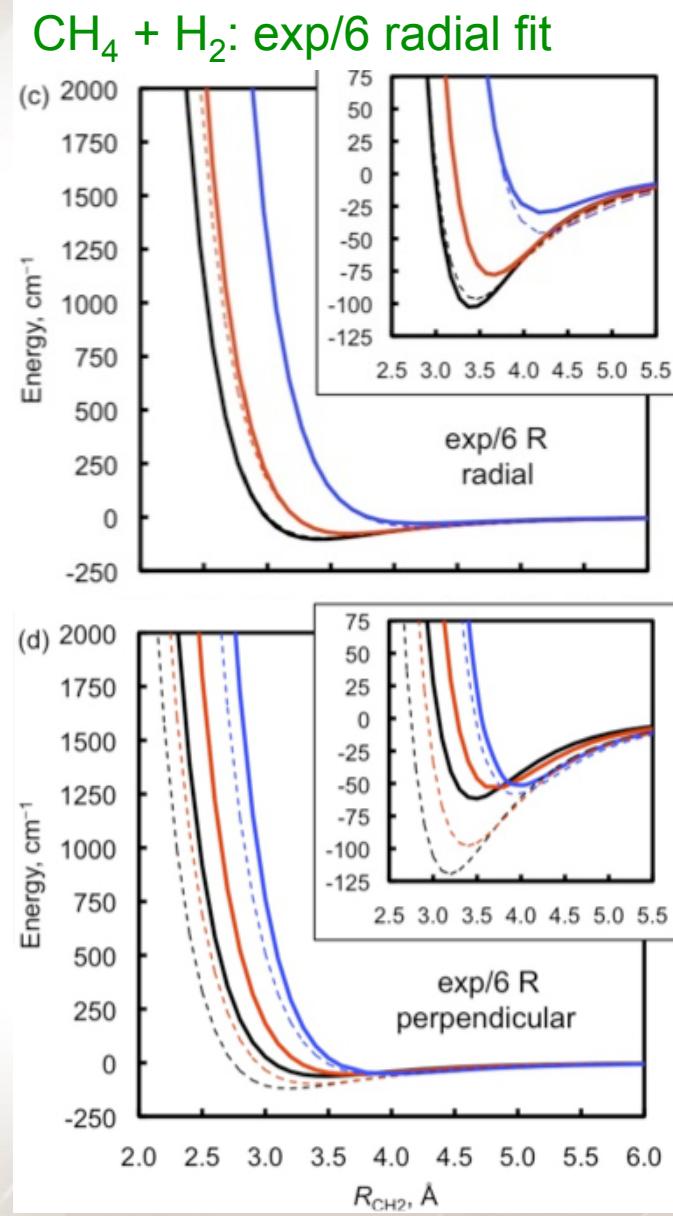




Fitting V_{int} for diatomic baths

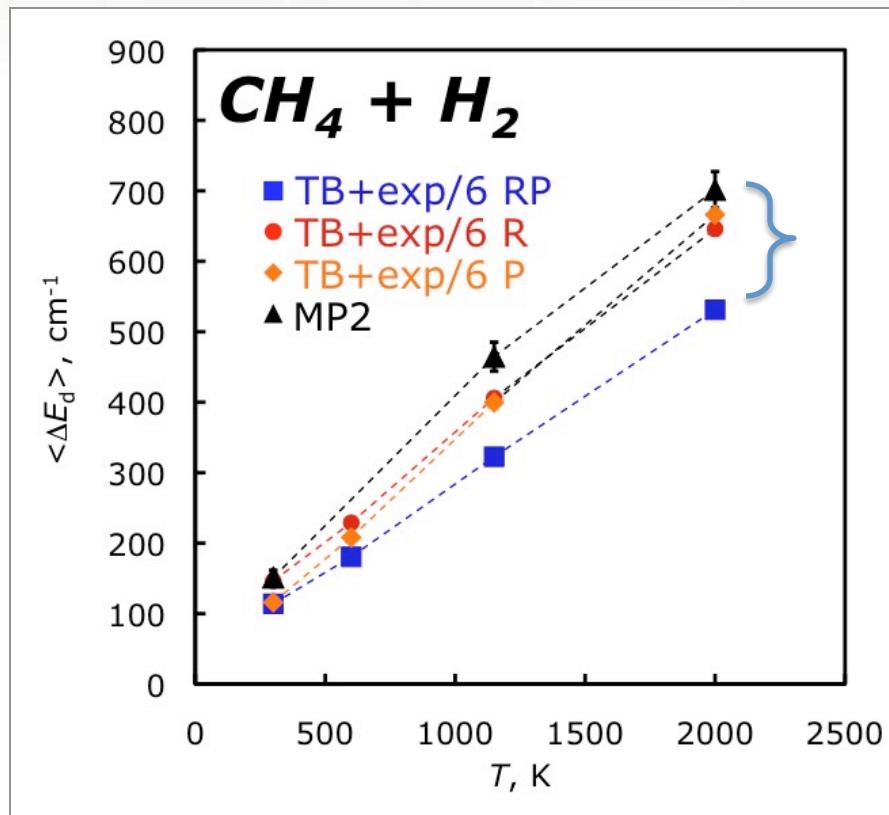


3 exp/6 parameterizations
were obtained: R, P, & RP





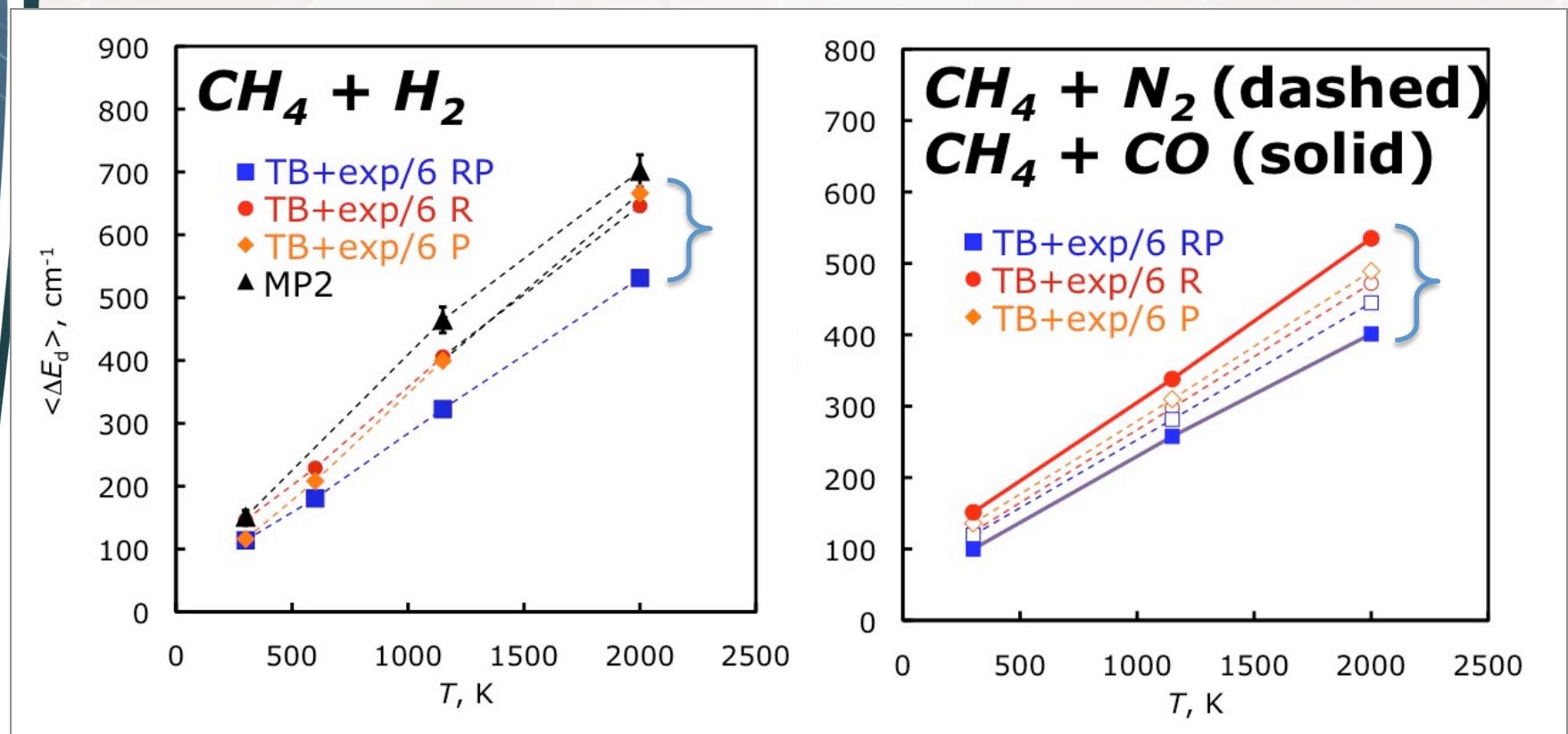
Tests of the separable pairwise method



- ✓ The compromise (RP) fit is the least accurate for H₂
- ✓ Uncertainties of 20-40% for diatomic baths
- ✓ The “pairwise” approximation fails for diatomic baths



Tests of the separable pairwise method

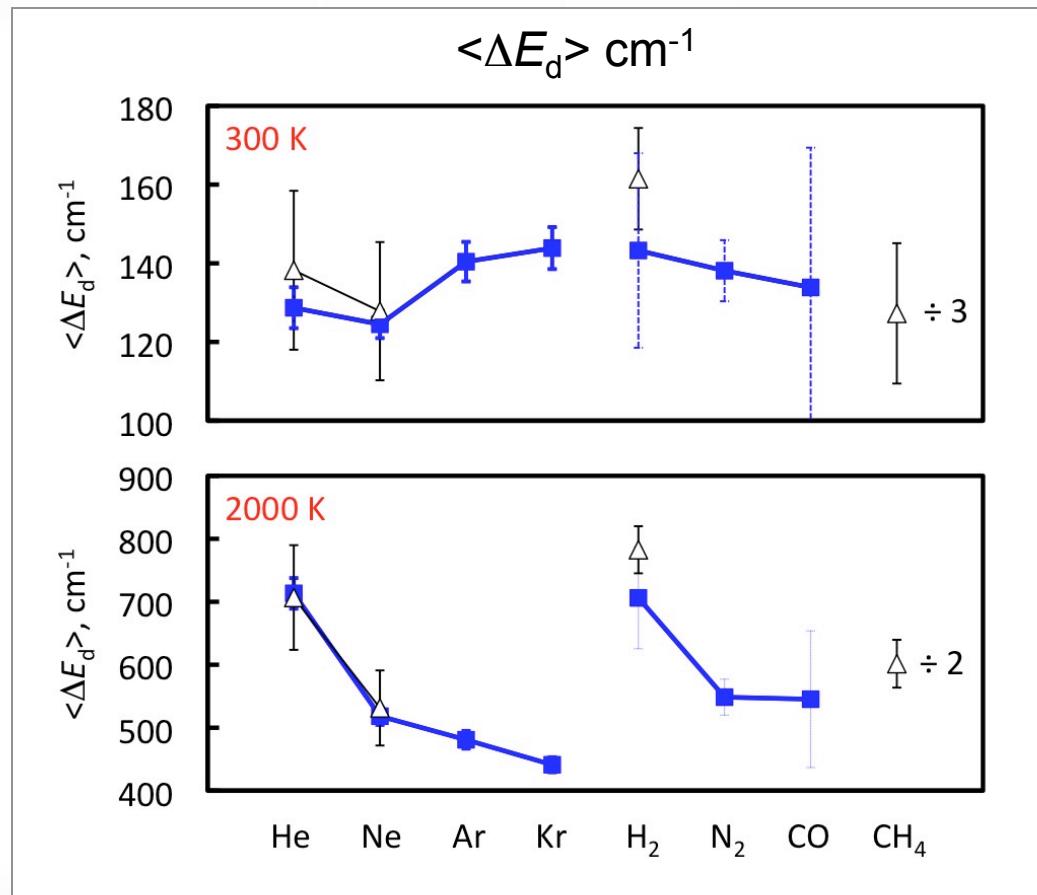


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Trends vs. the bath

CH_4 in eight baths (MP2 and TB+exp/6)

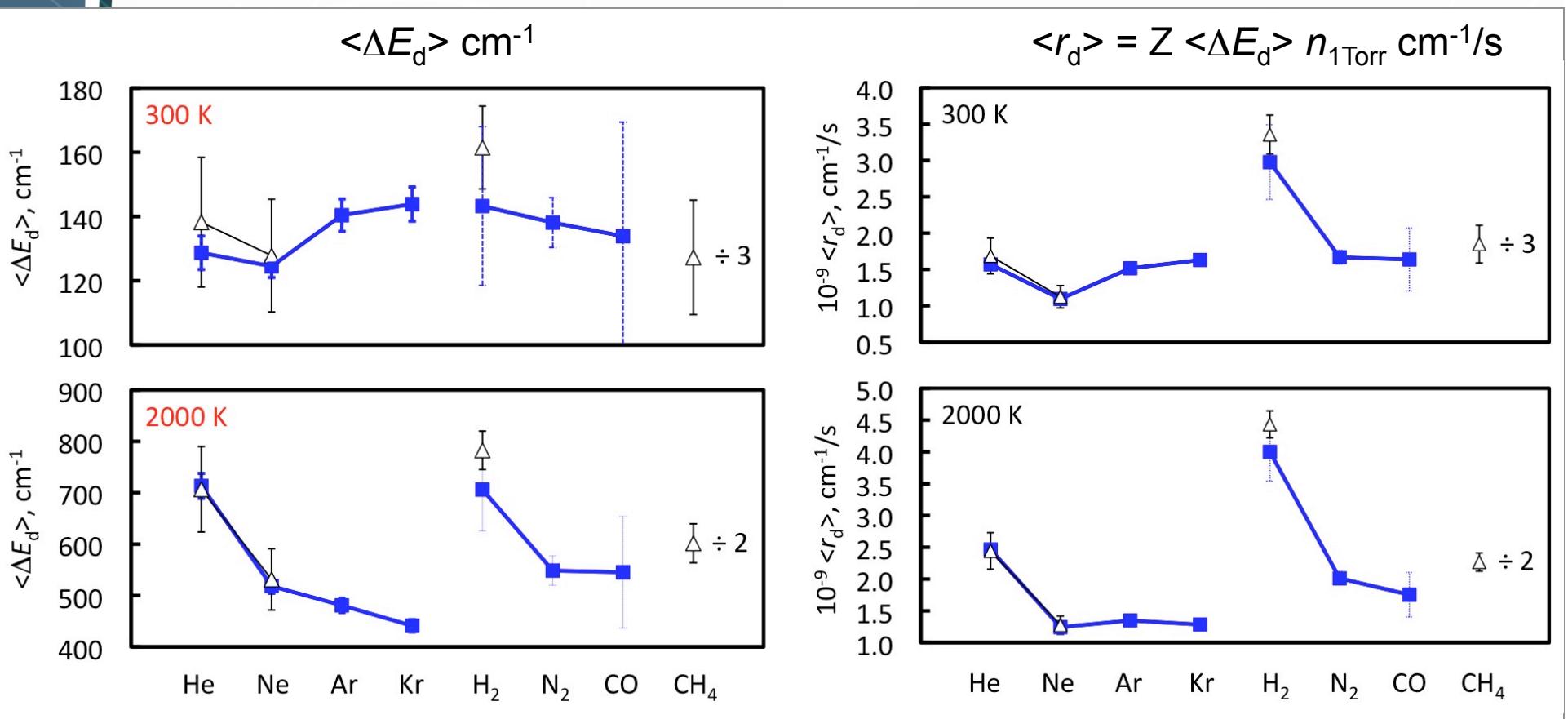


✓ Relative efficiencies are temperature dependent



Trends vs. the bath

$\text{CH}_4 + \text{M}$ for eight baths (MP2 and TB+exp/6)

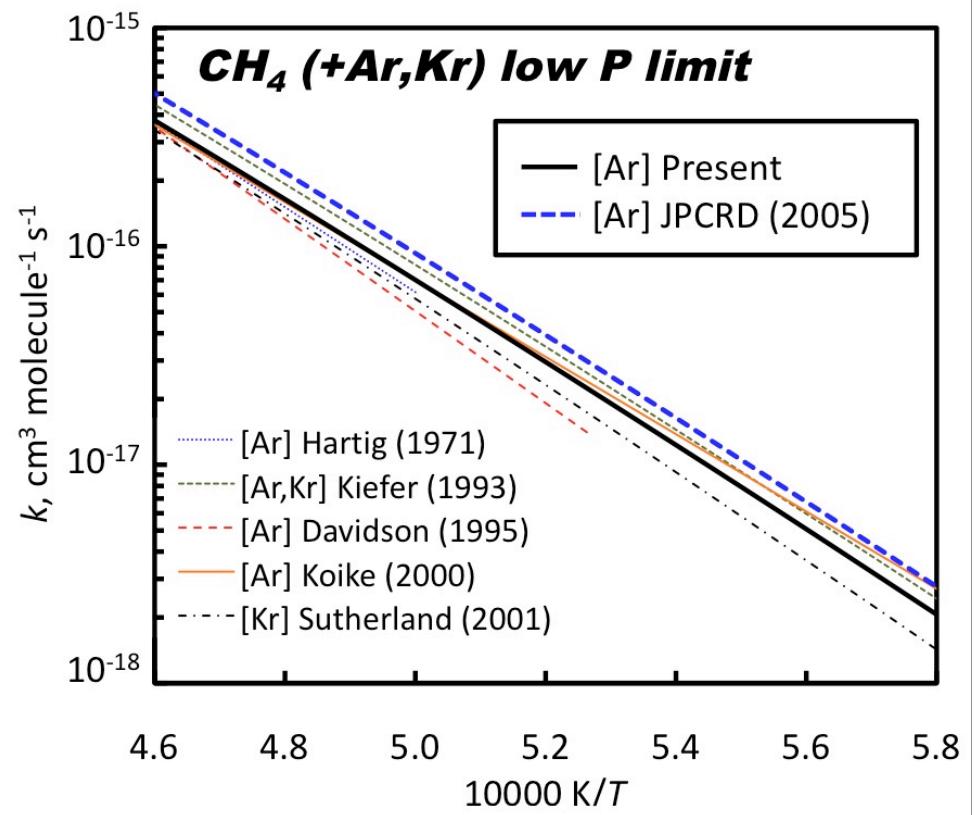
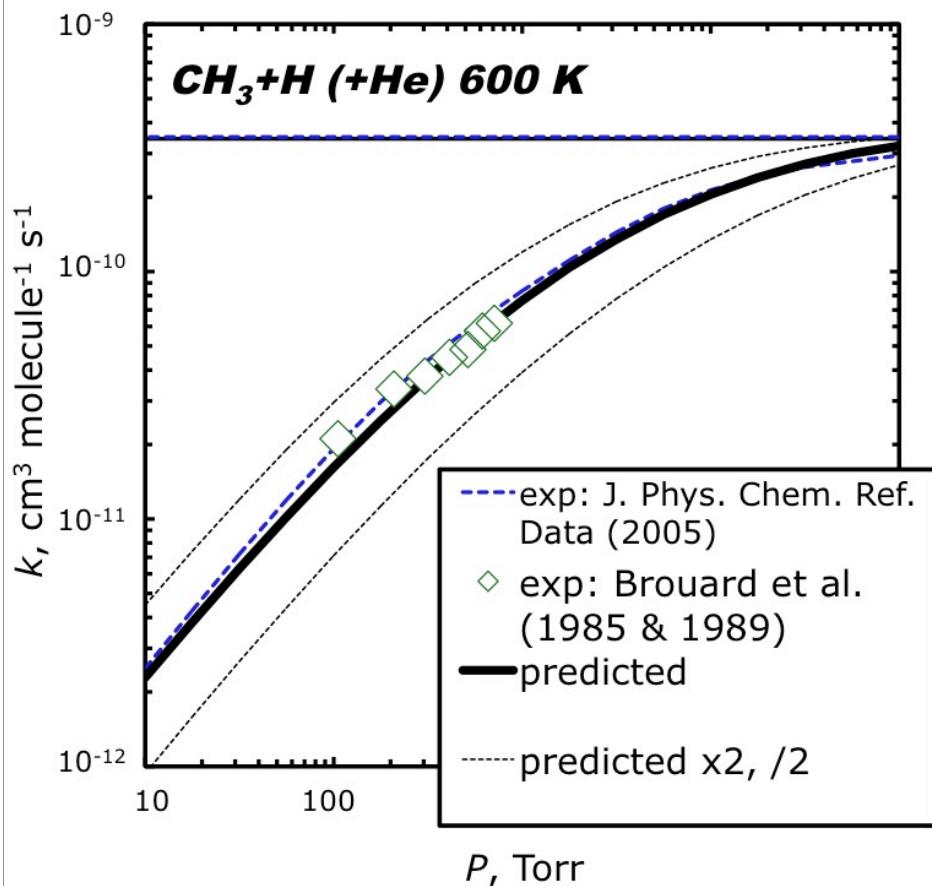


- ✓ Relative efficiencies are temperature dependent
- ✓ Trends in the energy transfer rate may be more relevant, apparent



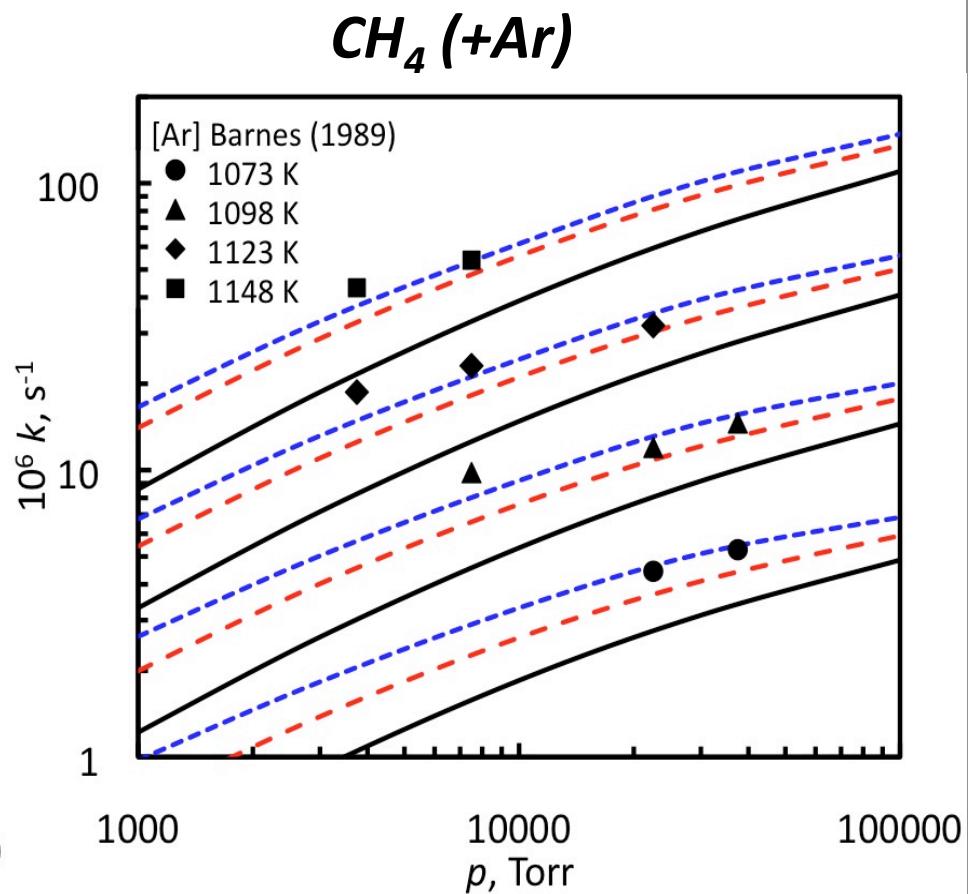
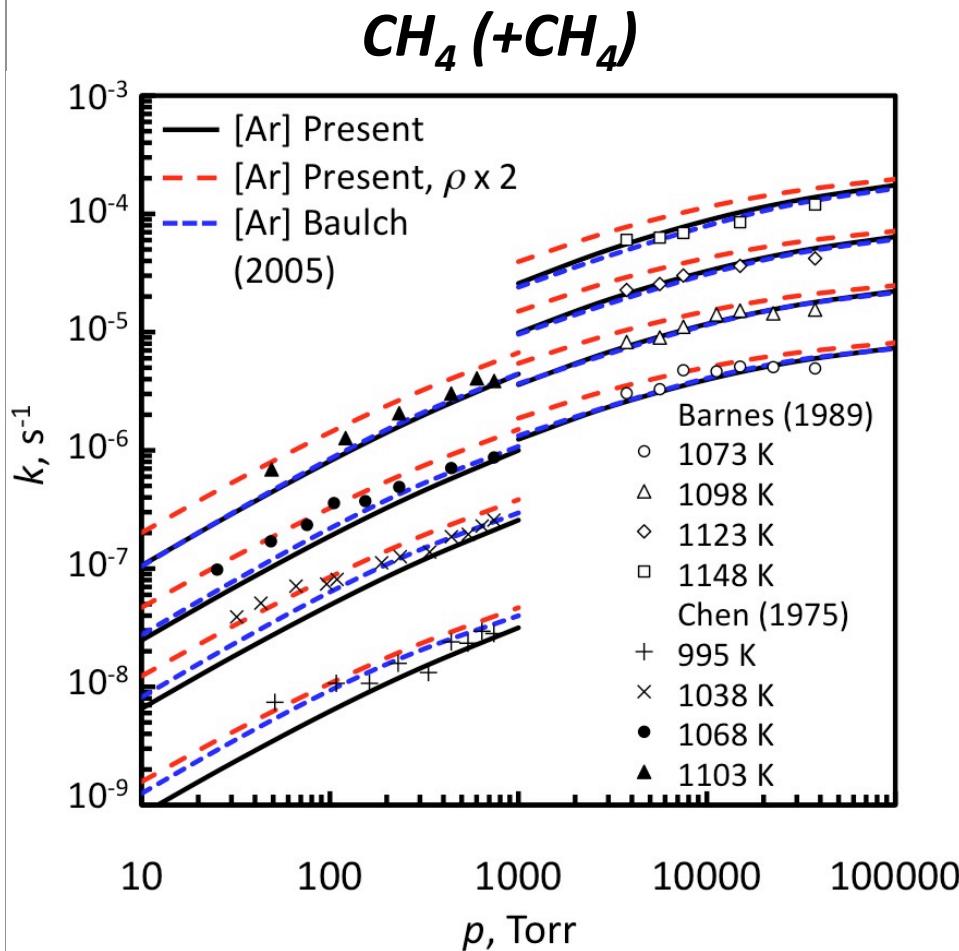
Accuracy of parameter-free kinetics

Test against low pressure & falloff measurements for $\text{CH}_4 + \text{M}$



Accuracy of parameter-free kinetics

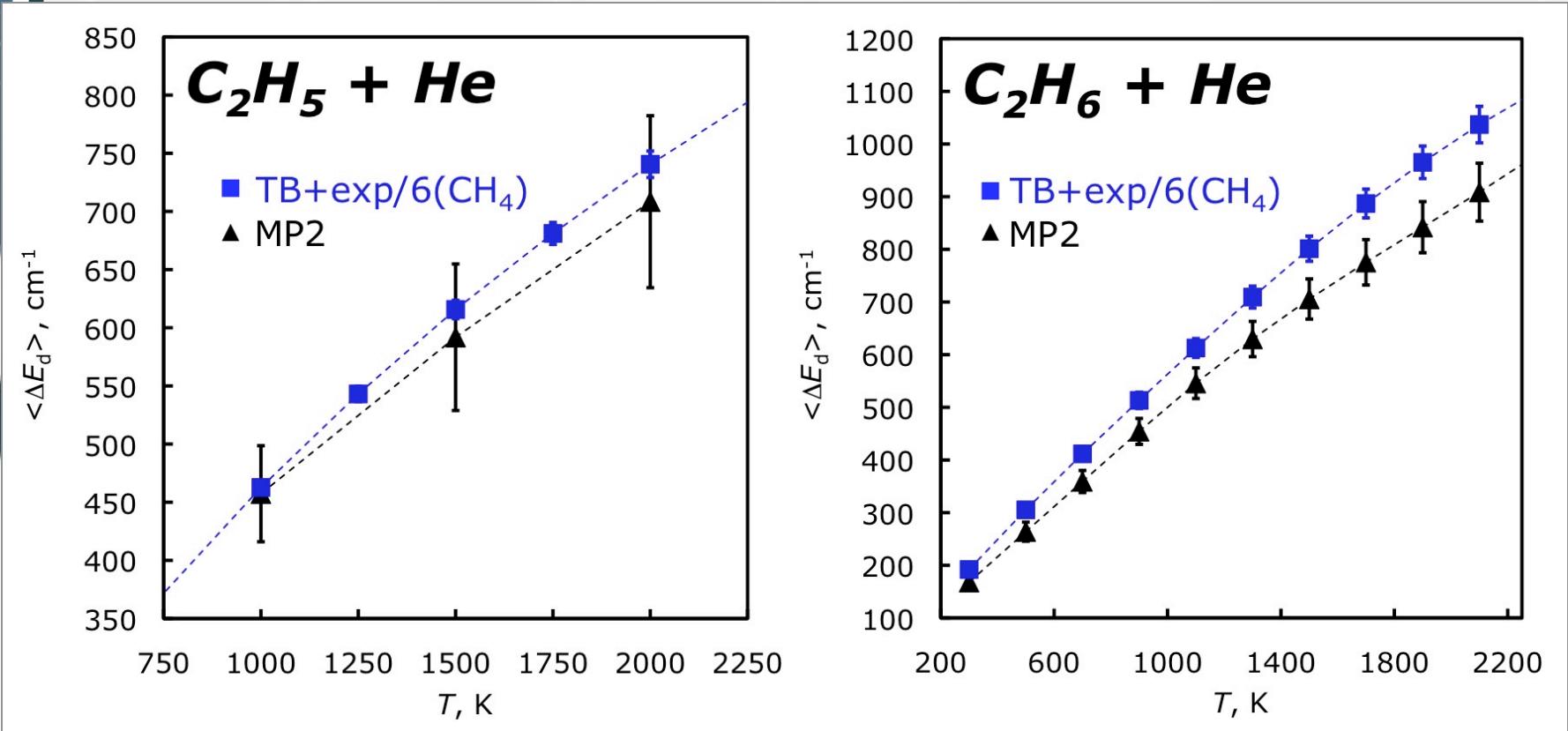
Vibrational anharmonicity approximately doubles k_0



- ✓ Experiments on the previous slide are better fit w/o anharmonicity
- ✓ Uncertainty due to anharmonicity > uncertainty in $\langle \Delta E_d \rangle$

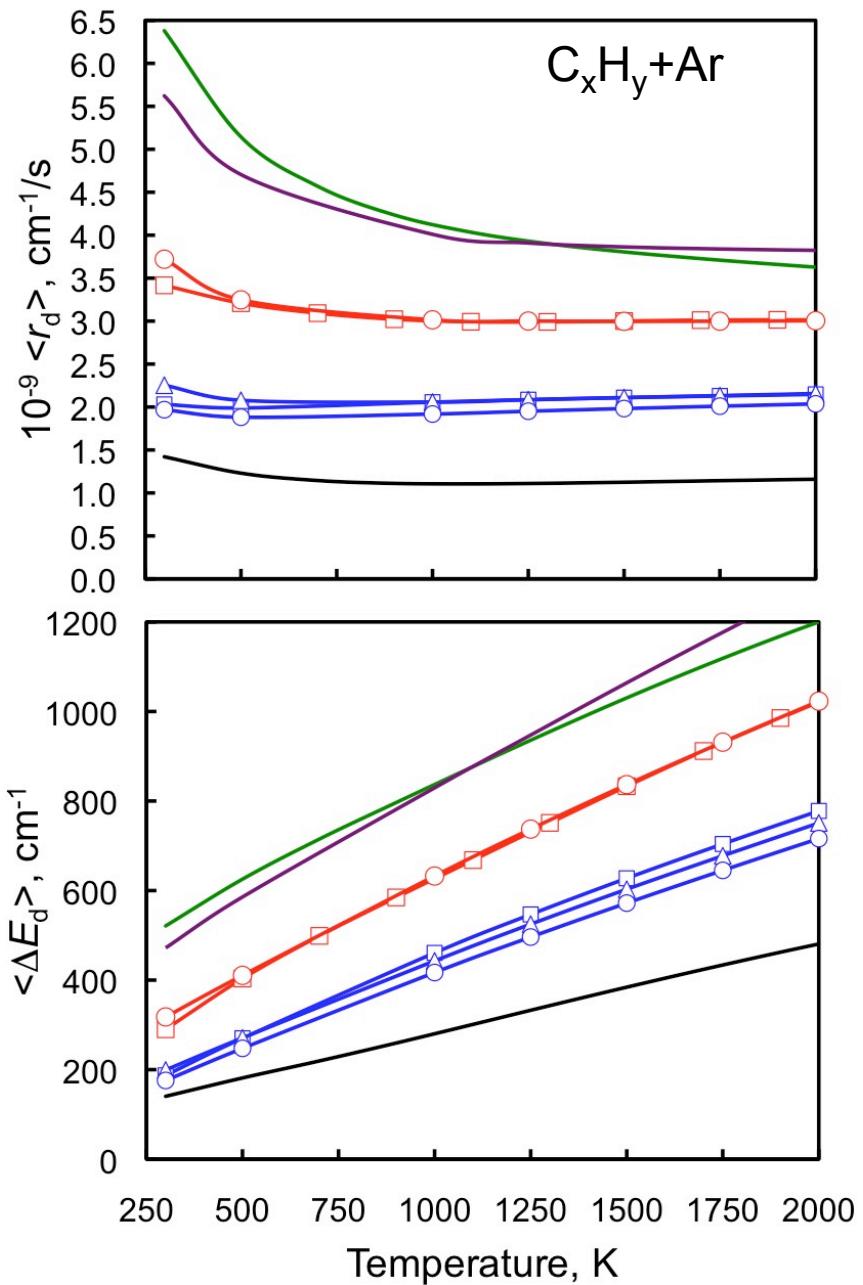


Test of “universal” exp/6 parameters



- ✓ “Universal” exp/6 parameters have errors of 0-15%
- ✓ The TB approximation for the target is again quite accurate
- ✓ The universal TB+exp/6 approach is efficient and readily applied to large systems

Trends vs. the target



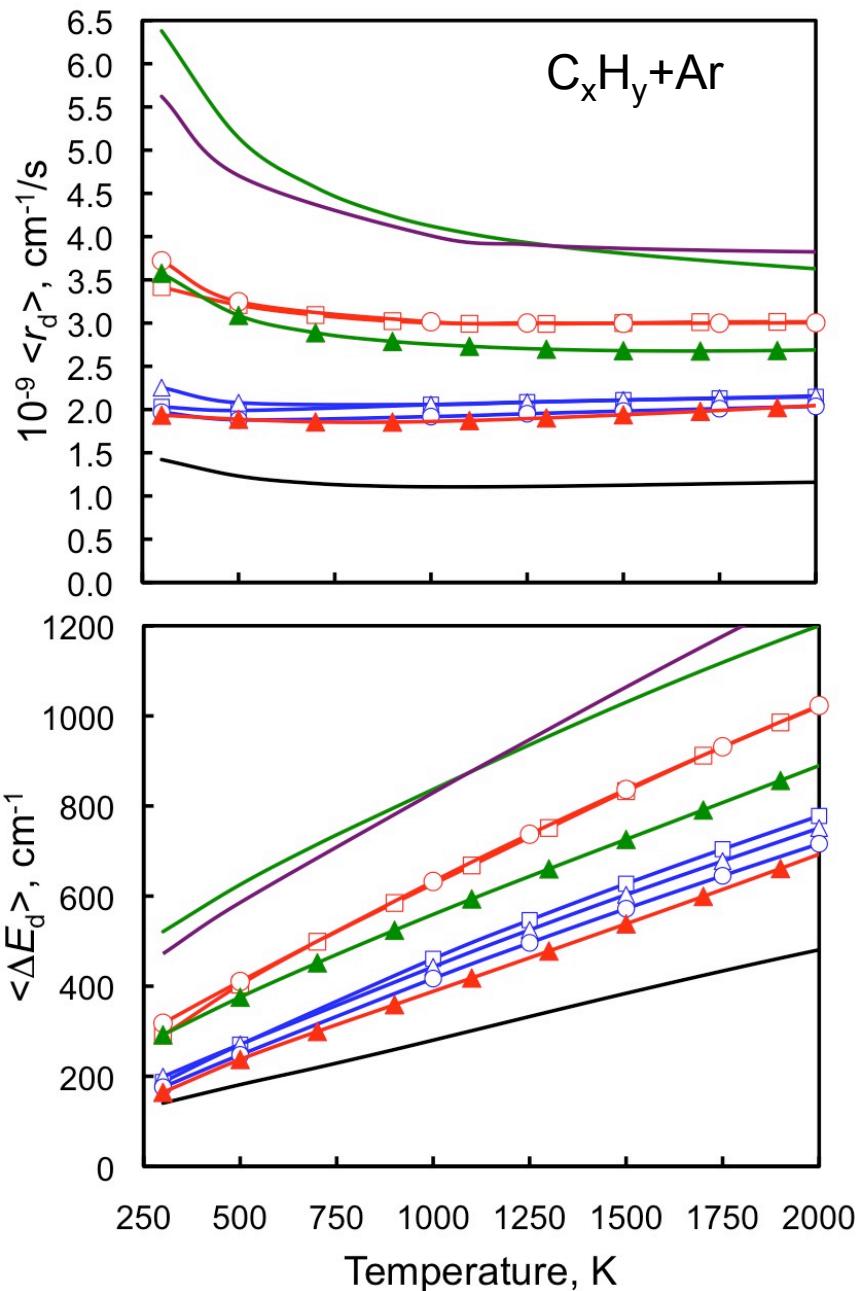
straight chain

- C6: 1-hexene
- C4: butane
- C3: propane, propyl
- C2: vinyl, ethyl, ethane
- C1: methane

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Trends vs. the target



↓
rings
 c-hexane
 c-propane

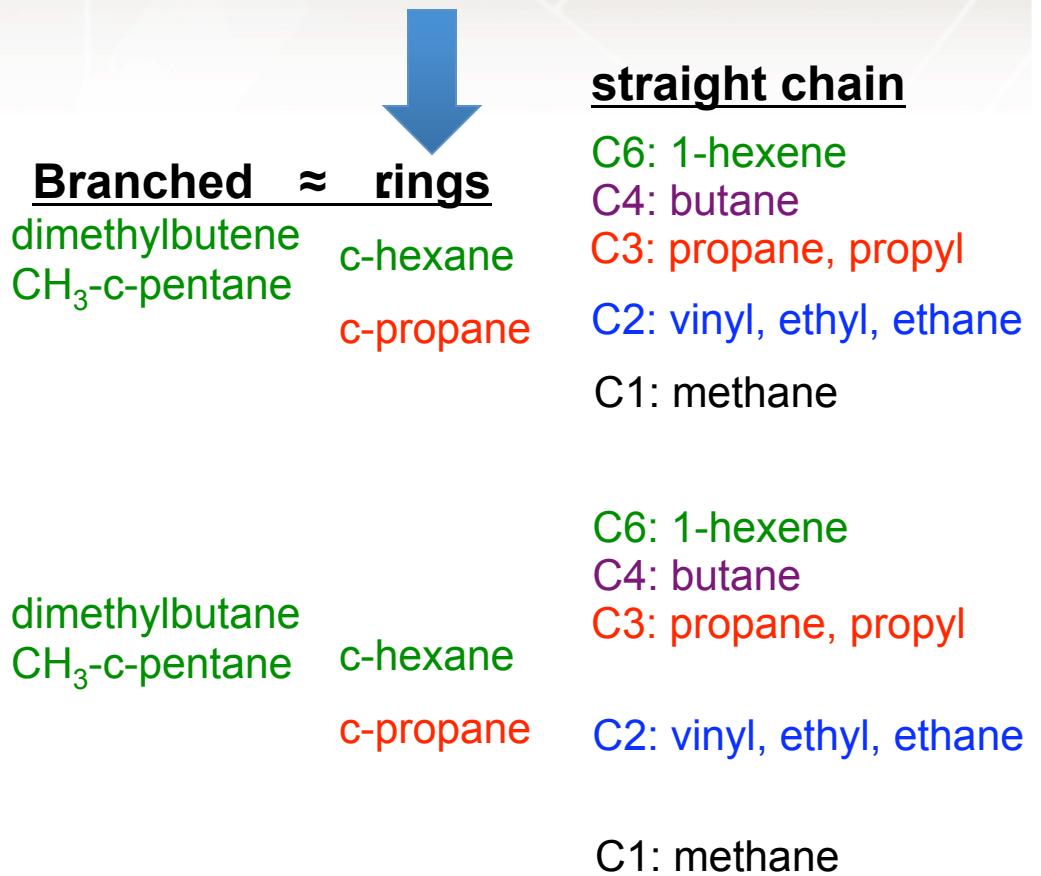
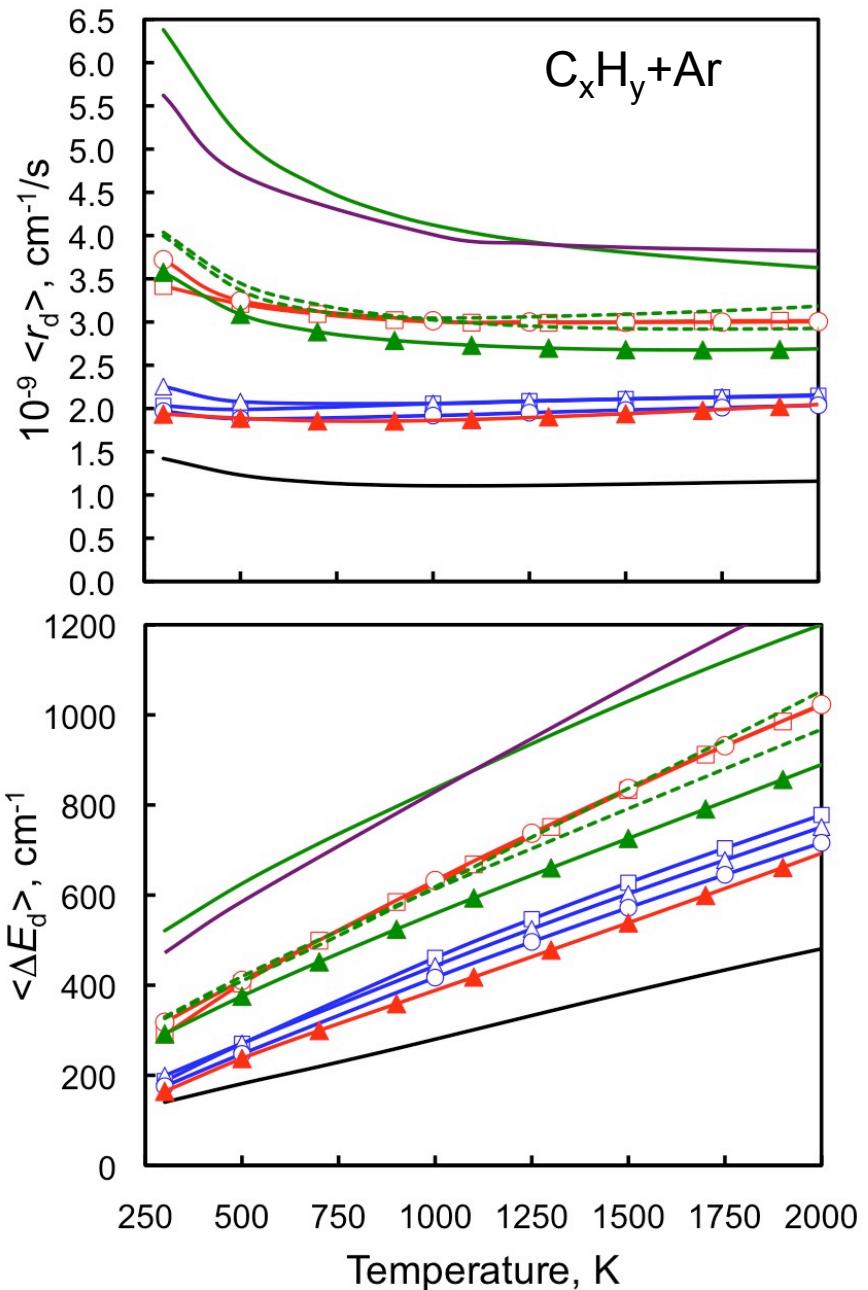
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Trends vs. the target





Conclusions

The treatment of the PES

- ✓ The separable pairwise approach
 - ✓ is accurate for atomic baths
 - ✓ with additional uncertainty for more complicated interaction PESs
- ✓ Universal TB+exp/6 parameterizations can be used to efficiently study complex systems

Predictive kinetics

- ✓ Trajectory-based evaluations of α and simple ET models can be accurate
- ✓ Quantitative kinetics will require accurate evaluations of vibrational partition functions and state densities

Trends

- ✓ Room temperature relative bath gas efficiencies may not be relevant at high T
- ✓ Systematic TB+exp/6 studies of hydrocarbons reveal fairly simple trends
- ✓ Group additivity schemes for estimating ET may be useful in developing detailed chemical kinetics models